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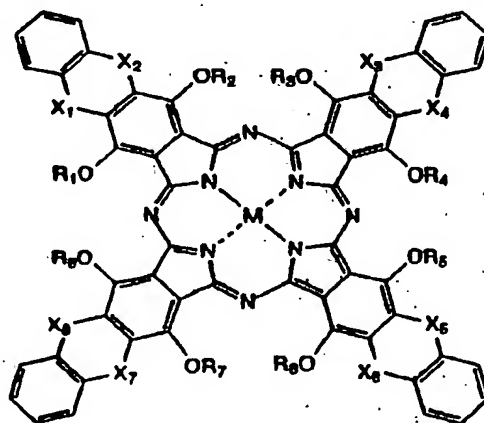
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(54) **Photothermal conversion material and planographic printing plate derived therefrom**

(57) A photothermal conversion material showing high sensitivity to the light of a semiconductor laser having an emission frequency band of 750 nm ~ 900 nm with a high photothermal conversion efficiency and a planographic original plate fabricated by using the transducer are provided. This photothermal conversion material comprises a phthalocyanine compound of the following general formula (I)



(I)

wherein $R_1 \sim R_8$ each represents alkyl or alkoxyalkyl; $X_1 \sim X_8$ each represents sulfur or NR_9 , where R_9 is hydrogen or alkyl.

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Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to a photothermal conversion material which absorbs laser light to generate heat.

BACKGROUND OF THE INVENTION

10 **[0002]** Keeping abreast with the recent advances in laser technology, studies have been undertaken on methods for converting laser radiation to the thermal energy necessary for recording, for example an image forming method utilizing a laser thermal recording material or a laser thermal transfer printing material for high-speed, high-density, high-image-quality recording or reproduction. Moreover, against the background of the wide-spread use of computers and rapidly developing electronics inclusive of improvements in digital image processing technology, development of the so-called computer-to-plate (CTP) technology for direct fabrication of printing plates from digital data is in progress.

15 **[0003]** In the technology comprising converting laser light to heat for image recording (laser thermal recording technology), a photothermal conversion material (light-to-heat converter) suited to the wavelength of a laser is used for conversion of absorbed laser light to heat to form an image but unless the laser output is raised to a fairly high level, the thermal energy required for image formation cannot be obtained. Therefore, there is a standing demand for development of a material having a high photothermal conversion efficiency.

20 **[0004]** The known CTP technology includes, as classified by plate fabrication methodology, the laser light exposure method, the writing method using a thermal head, the method for local voltage application using pin electrodes, and the ink jet method for forming an ink-repellent or -receptive layer, among others. The laser light exposure method, in particular, is superior to other methods in resolution and platemaking speed and in this field, therefore, a variety of image-forming techniques are being studied.

25 **[0005]** Today, compact, high-output, inexpensive semiconductor lasers having an emission band in the near-infrared region (750 nm ~ 900 nm) of the spectrum are readily available and can be exploited as exposure light sources in printing plate fabrication.

30 **[0006]** The plate fabricating method using laser light is either of the light-sensitive type or of the heat-sensitive type. The light-sensitive plate material is available either in the electrophotographic system using an organic photoconductor (OPC) or in the silver salt system utilizing a salt of silver but both materials have the disadvantage that a large-sized, expensive production equipment is required and that the cost of the plate is fairly high as compared with the conventional presensitized (PS) plate. Furthermore, there is the problem associated with disposal of the developer. Therefore, the above-mentioned plate materials have not been commercially implemented as yet.

35 **[0007]** The heat-sensitive plate material has the disadvantage of low sensitivity as compared with the light-sensitive plate material but has been energetically studied in view of the advantage that it can be handled under the interior (illuminated) conditions and the required equipment may be small and inexpensive.

[0008] The heat-sensitive plate materials invariably require the use of the so-called photothermal transducer for the conversion of light to heat.

40 **[0009]** It is essential that the photothermal conversion material absorb the laser light used, and for an enhanced sensitivity, its ability to absorb the laser light must be sufficiently high.

[0010] The light-to-heat converting substance for such a photothermal conversion material includes pigment type substances and dyestuff type substances. A typical pigment type substance is carbon black. As dyestuff type substances, a variety of substances have been proposed, although polymethine dyes are commonly employed. Carbon black offers a broad choice of compatible lasers but has the disadvantage that its ability to absorb laser light is generally so low compared with dyes that it must be used in large amounts. Moreover, a sophisticated dispersion technique is essential.

45 **[0011]** The dyestuff type substance must have a large capacity to absorb the emission of the semiconductor laser used, high compatibility with the concomitant image-forming component and resin binder, and high solubility in the solvent used.

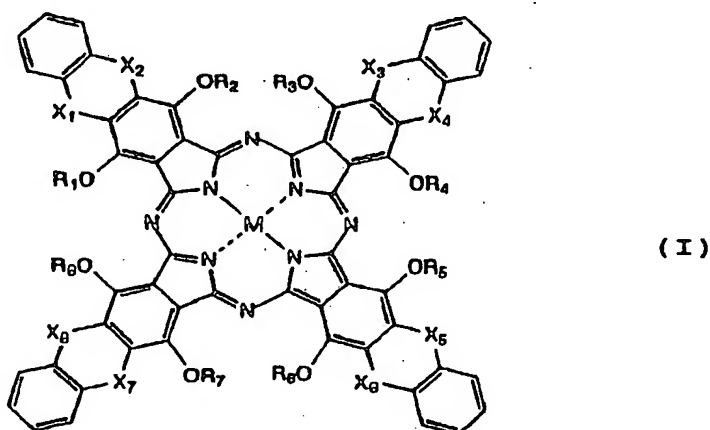
50 **[0012]** Polymethine dyes are essentially of the salt type so that the type of solvent that can be used is limited and the compatibility with the image forming component and resin binder is poor.

OBJECTS AND SUMMARY OF THE INVENTION

55 **[0013]** The present invention has for its object to provide a photothermal conversion material which has high sensitivity to semiconductor lasers having an emission band in the near-infrared region (750 nm ~ 900 nm) of the spectrum and can be used for high-speed, high-density, high-image-quality laser thermal recording. It is a further object of the invention to provide a planographic original plate for CTP use which is capable of giving prints with high image quality.

[0014] As the result of their extensive research for accomplishing the above objects, the inventors of the present invention discovered that a phthalocyanine compound having a herein-defined chemical structure can be used as a light-to-heat converting agent and gives a photothermal conversion material which has good sensitivity to laser light, high photothermal conversion efficiency, and good processability for various applications. The inventors have accordingly developed the present invention.

[0015] The present invention relates, in a first aspect thereof, to a photothermal conversion material comprising a phthalocyanine compound of the following general formula (I).



wherein $R_1 \sim R_8$ each represents alkyl or alkoxyalkyl; $X_1 \sim X_8$ each represents sulfur or NR_9 ; $X_1 = (\text{either } X_3 \text{ or } X_4) = (\text{either } X_5 \text{ or } X_6) = (\text{either } X_7 \text{ or } X_8) = \text{sulfur and } X_2 = (\text{the other one of } X_3 \text{ and } X_4) = (\text{the other one of } X_5 \text{ and } X_6) = (\text{the other one of } X_7 \text{ and } X_8) = NR_9$; R_9 represents hydrogen or alkyl; M represents a couple of hydrogen atoms, a divalent metal, a trivalent metal derivative, or a tetravalent metal derivative.

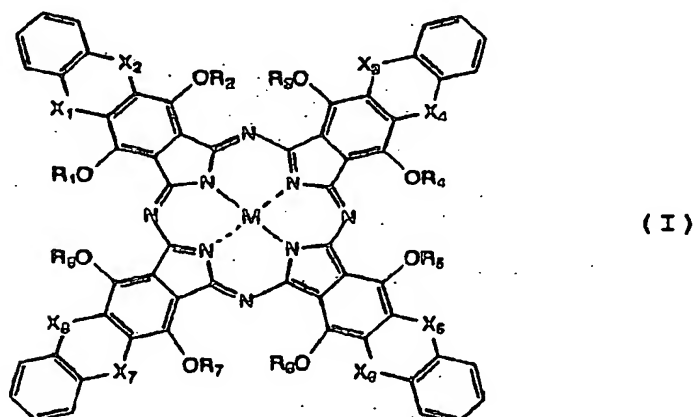
[0016] The present invention relates, in a second aspect thereof, to a planographic original plate for CTP use which comprises a support and, as disposed thereon, a photothermal conversion layer containing the photothermal conversion material according to said first aspect of the invention.

[0017] The present invention relates, in a third aspect thereof, to a method of fabricating a planographic printing plate which comprises exposing a planographic original plate according to said second aspect of the invention to light using a semiconductor laser having an emission band of 750 nm ~ 900 nm as a light source.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0018] The present invention is now described in detail.

[0019] The first aspect of the present invention is a photothermal conversion material containing a phthalocyanine compound of the following general formula (I).

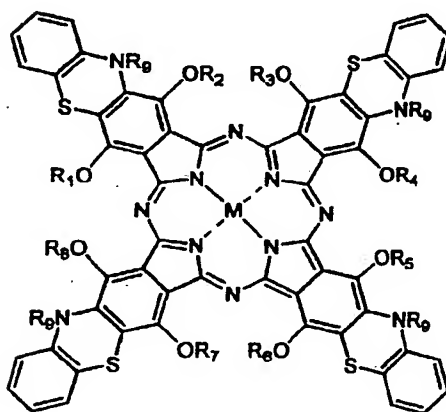


wherein $R_1 \sim R_8$ each represents alkyl or alkoxyalkyl; $X_1 \sim X_8$ each represents sulfur or NR_9 ; $X_1 = (\text{either } X_3 \text{ or } X_4) = (\text{either } X_5 \text{ or } X_6) = (\text{either } X_7 \text{ or } X_8) = \text{sulfur}$ and $X_2 = (\text{the other one of } X_3 \text{ and } X_4) = (\text{the other one of } X_5 \text{ and } X_6) = (\text{the other one of } X_7 \text{ and } X_8) = NR_9$; R_9 represents hydrogen or alkyl; M represents a couple of hydrogen atoms, a divalent metal, a trivalent metal derivative, or a tetravalent metal derivative.

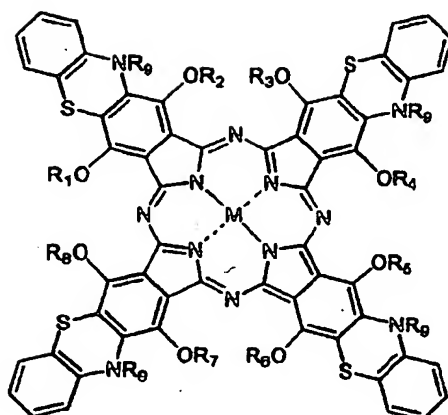
[0020] Thus, the photothermal conversion material according to this invention contains at least one member selected from among the phthalocyanine compounds of the following general formulas (Ia) ~ (Id).



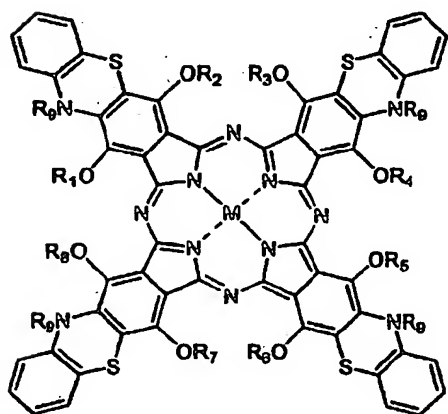
(Ia)



(Ib)



(I c)



(I d)

[0021] In the above respective formulas, $R_1 \sim R_8$ each represents alkyl or alkoxyalkyl; R_9 represents hydrogen or alkyl; M represents a couple of hydrogen atoms, a divalent metal, a trivalent metal derivative, or a tetravalent metal derivative.

[0022] When any of $R_1 \sim R_8$ represents alkyl, it is preferably a straight-chain or branched alkyl group of 1~12 carbon atoms and more preferably a straight-chain or branched alkyl group of 1~8 carbon atoms. To mention specific examples, it may be methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, neopentyl, n-hexyl, isohexyl, sec-hexyl, 2-ethylbutyl, n-heptyl, isoheptyl, sec-heptyl, n-octyl, 2-ethylhexyl, n-decyl, and n-dodecyl, among others.

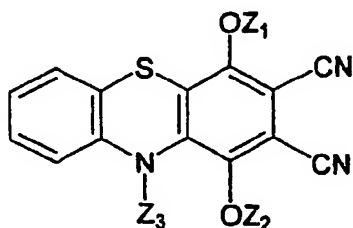
[0023] When any of $R_1 \sim R_8$ represents alkoxyalkyl, it is preferably a group containing a total of 2 to 6 carbon atoms, thus including methoxyethyl, methoxypropyl, methoxybutyl, ethoxyethyl, ethoxypropyl, ethoxybutyl, n-propoxyethyl, iso-propoxyethyl, and n-propoxypropyl, among others.

[0024] When R_9 is alkyl, it is preferably a straight-chain or branched alkyl group of 1~12 carbon atoms and more preferably a straight-chain or branched alkyl group of 1~8 carbon atoms. As specific examples, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, neopentyl, n-heptyl, isoheptyl, sec-heptyl, n-octyl, 2-ethylhexyl, n-decyl, and n-dodecyl can be mentioned. Thus, R_9 is preferably hydrogen or a straight-chain or branched alkyl group of 1~12 carbon atoms and more preferably hydrogen or a straight-chain or branched alkyl group of 1~8 carbon atoms.

[0025] When M represents a divalent metal, it is preferably Cu, Zn, Fe, Co, Ni, Ru, Pb, Rh, Pd, Pt, Mn, or Sn. The trivalent or tetravalent metal derivative is preferably $AlCl_3$, $InCl_3$, $FeCl_3$, $MnOH$, $SiCl_4$, $SnCl_4$, $GeCl_4$, $Si(OH)_4$, $Sn(OH)_4$, $Ge(OH)_4$, VO, or TiO_2 . In particular, M is preferably Co, Ni, Cu, Zn, VO, or TiO_2 .

[0026] The phthalocyanine compound of general formula (I) for use in the present invention can be produced, for example by reacting a phthalonitrile compound of the following general formula (II) with either a metal or a metal

derivative in a suitable solvent, preferably in an organic solvent having a boiling point not below 130°C, at a temperature of 100~300°C.



(II)

wherein Z_1 and Z_2 each represents the same alkyl or alkoxyalkyl group as defined for R_1 ~ R_8 ; Z_3 represents hydrogen or the same alkyl group as defined for R_9 .

[0027] Table 1 is a list of preferred examples of the compound of general formula (I) which can be used in the present invention.

[0028] The compounds shown in Table 1 are those compounds of formula (I) wherein R_1 = (either R_3 or R_4) = (either R_5 or R_6) = (either R_7 or R_8) and R_2 = (the other one of R_3 and R_4) = (the other one of R_5 and R_6) = (the other one of R_7 and R_8).

TABLE 1

Compound Nos.	M	R_1	R_2	R_9
(1)	Cu	CH ₃	CH ₃	H
(2)	Cu	CH ₃	CH ₃	n-C ₆ H ₁₃
(3)	Cu	C ₂ H ₅	C ₂ H ₅	n-C ₅ H ₁₁
(4)	Cu	n-C ₃ H ₇	n-C ₃ H ₇	n-C ₆ H ₁₃
(5)	Cu	iso-C ₃ H ₇	iso-C ₃ H ₇	n-C ₅ H ₁₁
(6)	Zn	n-C ₄ H ₉	n-C ₄ H ₉	H
(7)	—	FeCl	n-C ₄ H ₉	CH ₃
(8)	Co	n-C ₄ H ₉	n-C ₄ H ₉	C ₂ H ₅
(9)	Ni	n-C ₄ H ₉	n-C ₄ H ₉	n-C ₄ H ₉
(10)	Pd	n-C ₄ H ₉	n-C ₄ H ₉	n-C ₆ H ₁₃
(11)	MnOH	iso-C ₄ H ₉	iso-C ₄ H ₉	H
(12)	VO	iso-C ₄ H ₉	iso-C ₄ H ₉	n-C ₃ H ₇
(13)	Ru	iso-C ₄ H ₉	iso-C ₄ H ₉	C ₂ H ₅
(14)	Rh	iso-C ₄ H ₉	iso-C ₄ H ₉	n-C ₄ H ₉
(15)	Pt	iso-C ₄ H ₉	iso-C ₄ H ₉	n-C ₅ H ₁₁
(16)	AlCl	sec-C ₄ H ₉	sec-C ₄ H ₉	H
(17)	InCl	sec-C ₄ H ₉	sec-C ₄ H ₉	CH ₃
(18)	Zn	sec-C ₄ H ₉	sec-C ₄ H ₉	C ₂ H ₅
(19)	Ni	sec-C ₄ H ₉	sec-C ₄ H ₉	n-C ₄ H ₉
(20)	FeCl	sec-C ₄ H ₉	sec-C ₄ H ₉	n-C ₆ H ₁₃
(21)	SiCl ₂	n-C ₅ H ₁₁	n-C ₅ H ₁₁	H
(22)	Cu	n-C ₅ H ₁₁	n-C ₅ H ₁₁	n-C ₃ H ₇
(23)	TiO	n-C ₅ H ₁₁	n-C ₅ H ₁₁	C ₂ H ₅
(24)	VO	n-C ₅ H ₁₁	n-C ₅ H ₁₁	n-C ₅ H ₁₁
(25)	Pd	n-C ₅ H ₁₁	n-C ₅ H ₁₁	n-C ₆ H ₁₃
(26)	Pb	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	H
(27)	Cu	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	H
(28)	Zn	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	H
(29)	FeCl	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	H
(30)	Co	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	H

TABLE 1 (continued)

Compound Nos.	M	R ₁	R ₂	R ₉
(31)	Ni	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	H
(32)	Pd	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	H
(33)	MnOH	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	H
(34)	VO	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	H
(35)	Cu	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	CH ₃
(36)	Cu	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	C ₂ H ₅
(37)	Zn	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	C ₂ H ₅
(38)	Pb	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	C ₂ H ₅
(39)	Co	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	C ₂ H ₅
(40)	Ni	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	C ₂ H ₅
(41)	Pd	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	C ₂ H ₅
(42)	MnOH	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	C ₂ H ₅
(43)	VO	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	C ₂ H ₅
(44)	Co	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	n-C ₄ H ₉
(45)	Ru	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	n-C ₆ H ₁₃
(46)	SnCl ₂	n-C ₆ H ₁₃	n-C ₆ H ₁₃	H
(47)	Zn	n-C ₆ H ₁₃	n-C ₆ H ₁₃	CH ₃
(48)	Pt	n-C ₆ H ₁₃	n-C ₆ H ₁₃	n-C ₃ H ₇
(49)	Ni	n-C ₆ H ₁₃	n-C ₆ H ₁₃	n-C ₅ H ₁₁
(50)	Pd	n-C ₆ H ₁₃	n-C ₆ H ₁₃	n-C ₆ H ₁₃
(51)	GeCl ₂	iso-C ₆ H ₁₃	iso-C ₆ H ₁₃	H
(52)	FeCl	iso-C ₆ H ₁₃	iso-C ₆ H ₁₃	CH ₃
(53)	Cu	iso-C ₆ H ₁₃	iso-C ₆ H ₁₃	C ₂ H ₅
(54)	VO	iso-C ₆ H ₁₃	iso-C ₆ H ₁₃	n-C ₄ H ₉
(55)	Zn	iso-C ₆ H ₁₃	iso-C ₆ H ₁₃	n-C ₆ H ₁₃
(56)	Si(OH) ₂	n-C ₇ H ₁₅	n-C ₇ H ₁₅	H
(57)	Rh	n-C ₇ H ₁₅	n-C ₇ H ₁₅	CH ₃
(58)	Zn	n-C ₇ H ₁₅	n-C ₇ H ₁₅	n-C ₃ H ₇
(59)	Ni	n-C ₇ H ₁₅	n-C ₇ H ₁₅	n-C ₄ H ₉
(60)	Co	n-C ₇ H ₁₅	n-C ₇ H ₁₅	n-C ₅ H ₁₁
(61)	Sn(OH) ₂	iso-C ₇ H ₁₅	iso-C ₇ H ₁₅	H
(62)	MnOH	iso-C ₇ H ₁₅	iso-C ₇ H ₁₅	CH ₃
(63)	TiO	iso-C ₇ H ₁₅	iso-C ₇ H ₁₅	C ₂ H ₅
(64)	Pb	iso-C ₇ H ₁₅	iso-C ₇ H ₁₅	n-C ₅ H ₁₁
(65)	Mg	iso-C ₇ H ₁₅	iso-C ₇ H ₁₅	n-C ₆ H ₁₃
(66)	Cu	n-C ₈ H ₁₇	n-C ₈ H ₁₇	H
(67)	Ge(OH) ₂	n-C ₈ H ₁₇	n-C ₈ H ₁₇	CH ₃
(68)	InCl	n-C ₈ H ₁₇	n-C ₈ H ₁₇	C ₂ H ₅
(69)	Zn	n-C ₈ H ₁₇	n-C ₈ H ₁₇	n-C ₃ H ₇
(70)	FeCl	n-C ₈ H ₁₇	n-C ₈ H ₁₇	n-C ₆ H ₁₃
(71)	Cu	CH ₃ OC ₂ H ₄	CH ₃ OC ₂ H ₄	H
(72)	Zn	CH ₃ OC ₂ H ₄	CH ₃ OC ₂ H ₄	H
(73)	FeCl	CN ₃ OC ₂ N ₄	CH ₃ OC ₂ H ₄	H
(74)	Co	CH ₃ OC ₂ H ₄	CH ₃ OC ₂ H ₄	H
(75)	Ni	CH ₃ OC ₂ H ₄	CH ₃ OC ₂ H ₄	H
(76)	Pd	CH ₃ OC ₂ H ₄	CH ₃ OC ₂ H ₄	H
(77)	MnOH	CH ₃ OC ₂ H ₄	CH ₃ OC ₂ H ₄	H
(78)	VO	CH ₃ OC ₂ H ₄	CH ₃ OC ₂ H ₄	H
(79)	TiO	CH ₃ OC ₂ H ₄	CH ₃ OC ₂ H ₄	CH ₃
(80)	AlCl	CH ₃ OC ₂ H ₄	CH ₃ OC ₂ H ₄	C ₂ H ₅

TABLE 1 (continued)

Compound Nos.	M	R ₁	R ₂	R ₉
(81)	InCl	CH ₃ OC ₂ H ₄	CH ₃ OC ₂ H ₄	n-C ₃ H ₇
(82)	MnOH	CH ₃ OC ₂ H ₄	CH ₃ OC ₂ H ₄	n-C ₅ H ₁₁
(83)	VO	CH ₃ OC ₃ H ₆	CH ₃ OC ₃ H ₆	H
(84)	Pd	CH ₃ OC ₃ H ₆	CH ₃ OC ₃ H ₆	CH ₃
(85)	Zn	CH ₃ OC ₃ H ₆	CH ₃ OC ₃ H ₆	C ₂ H ₅
(86)	FeCl	CH ₃ OC ₃ H ₆	CH ₃ OC ₃ H ₆	n-C ₄ H ₉
(87)	Co	CH ₃ OC ₃ H ₆	CH ₃ OC ₃ H ₆	n-C ₆ H ₁₃
(88)	Ni	CH ₃ OC ₄ H ₈	CH ₃ OC ₄ H ₈	H
(89)	Cu	CH ₃ OC ₄ H ₈	CH ₃ OC ₄ H ₈	CH ₃
(90)	Pb	CH ₃ OC ₄ H ₈	CH ₃ OC ₄ H ₈	C ₂ H ₅
(91)	Ru	CH ₃ OC ₄ H ₈	CH ₃ OC ₄ H ₈	n-C ₃ H ₇
(92)	Rh	CH ₃ OC ₄ H ₈	CH ₃ OC ₄ H ₈	n-C ₅ H ₁₁
(93)	VO	C ₂ H ₅ OC ₂ H ₄	C ₂ H ₅ OC ₂ H ₄	H
(94)	Ru	C ₂ H ₅ OC ₂ H ₄	C ₂ H ₅ OC ₂ H ₄	CH ₃
(95)	Rh	C ₂ H ₅ OC ₂ H ₄	C ₂ H ₅ OC ₂ H ₄	C ₂ H ₅
(96)	Pd	C ₂ H ₅ OC ₂ H ₄	C ₂ H ₅ OC ₂ H ₄	n-C ₄ H ₉
(97)	Pt	C ₂ H ₅ OC ₂ H ₄	C ₂ H ₅ OC ₂ H ₄	n-C ₆ H ₁₃
(98)	SiCl ₂	n-C ₃ H ₇ OC ₂ H ₄	n-C ₃ H ₇ OC ₂ H ₄	H
(99)	Cu	n-C ₃ H ₇ OC ₂ H ₄	n-C ₃ H ₇ OC ₂ H ₄	CH ₃
(100)	Zn	n-C ₃ H ₇ OC ₂ H ₄	n-C ₃ H ₇ OC ₂ H ₄	C ₂ H ₅
(101)	FeCl	iso-C ₃ H ₇ OC ₂ H ₄	iso-C ₃ H ₇ OC ₂ H ₄	n-C ₃ H ₇
(102)	Co	iso-C ₃ H ₇ OC ₂ H ₄	iso-C ₃ H ₇ OC ₂ H ₄	n-C ₅ H ₁₁
(103)	MnOH	C ₂ H ₅ OC ₃ H ₆	C ₂ H ₅ OC ₃ H ₆	H
(104)	VO	C ₂ H ₅ OC ₃ H ₆	C ₂ H ₅ OC ₃ H ₆	CH ₃
(105)	TiO	C ₂ H ₅ OC ₃ H ₆	C ₂ H ₅ OC ₃ H ₆	C ₂ H ₅
(106)	AlCl	C ₂ H ₅ OC ₃ H ₆	C ₂ H ₅ OC ₃ H ₆	n-C ₄ H ₉
(107)	InCl	C ₂ H ₅ OC ₃ H ₆	C ₂ H ₅ OC ₃ H ₆	n-C ₆ H ₁₃
(108)	CU	C ₂ H ₅ OC ₄ H ₈	C ₂ H ₅ OC ₄ H ₈	H
(109)	Cu	C ₂ H ₅ OC ₄ H ₈	C ₂ H ₅ OC ₄ H ₈	CH ₃
(110)	Ni	C ₂ H ₅ OC ₄ H ₈	C ₂ H ₅ OC ₄ H ₈	C ₂ H ₅
(111)	Zn	C ₂ H ₅ OC ₄ H ₈	C ₂ H ₅ OC ₄ H ₈	n-C ₃ H ₇
(112)	Co	C ₂ H ₅ OC ₄ H ₈	C ₂ H ₅ OC ₄ H ₈	n-C ₅ H ₁₁
(113)	Cu	C ₂ H ₅	n-C ₃ H ₇	H
(114)	Cu	C ₂ H ₅	n-C ₆ H ₁₃	CH ₃
(115)	Cu	C ₂ H ₅	n-C ₈ H ₁₇	C ₂ H ₅
(116)	Cu	C ₂ H ₅	n-C ₁₀ H ₂₁	n-C ₄ H ₉
(117)	Cu	C ₂ H ₅	n-C ₁₂ H ₂₅	n-C ₆ H ₁₃
(118)	Ni	iso-C ₅ H ₁₁	C ₂ H ₅	H
(119)	Co	iso-C ₅ H ₁₁	n-C ₄ H ₉	CH ₃
(120)	Zn	iso-C ₅ H ₁₁	n-C ₆ H ₁₃	C ₂ H ₅
(121)	VO	iso-C ₅ H ₁₁	n-C ₇ H ₁₅	n-C ₃ H ₇
(122)	MnOH	iso-C ₅ H ₁₁	n-C ₁₂ H ₂₅	n-C ₅ H ₁₁
(123)	Cu	iso-C ₅ H ₁₁	CH ₃ OC ₂ H ₄	H
(124)	Zn	iso-C ₅ H ₁₁	CH ₃ OC ₂ H ₄	H
(125)	FeCl	iso-C ₅ H ₁₁	CH ₃ OC ₂ H ₄	H
(126)	Co	iso-C ₅ H ₁₁	CH ₃ OC ₂ H ₄	H
(127)	Ni	iso-C ₅ H ₁₁	CH ₃ OC ₂ H ₄	H
(128)	Pd	iso-C ₅ H ₁₁	CH ₃ OC ₂ H ₄	H
(129)	MnOH	iso-C ₅ H ₁₁	CH ₃ OC ₂ H ₄	H
(130)	VO	iso-C ₅ H ₁₁	CH ₃ OC ₂ H ₄	H

TABLE 1 (continued)

Compound Nos.	M	R ₁	R ₂	R ₉
(131)	Cu	iso-C ₅ H ₁₁	CH ₃ OC ₃ H ₆	CH ₃
(132)	AlCl	iso-C ₅ H ₁₁	CH ₃ OC ₄ H ₈	C ₂ H ₅
(133)	InCl	iso-C ₅ H ₁₁	C ₂ H ₅ OC ₂ H ₄	n-C ₁₀ H ₂₁
(134)	Ni	iso-C ₅ H ₁₁	C ₂ H ₅ OC ₄ H ₈	n-C ₁₂ H ₂₅
(135)	H ₂	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	H
(136)	VO	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	n-C ₄ H ₉
(137)	VO	iso-C ₅ H ₁₁	iso-C ₅ H ₁₁	n-C ₈ H ₁₇

[0029] The phthalocyanine compound of general formula (I) is a known compound and the compound as such is described in Japanese Kokai Tokkyo Koho HB-60008. The inventors of the present invention explored into the photo-thermal conversion characteristic of the compound and found that, among various materials absorbing in the near-infrared region of the spectrum, the particular compound has exceedingly high sensitivity to laser light exhibiting a high photothermal conversion efficiency and can be applied with advantage, for example, to laser thermal transfer printing and laser thermal recording materials conducive to high-speed recording and giving high-density, high-image-quality records.

[0030] Furthermore, because the phthalocyanine compound of general formula (I) is very readily soluble in various solvents which are generally used in the construction of the photothermal conversion layer of a planographic original plate for CTP use and well compatible with various kinds of binder resins, it can be easily formulated into coating dopes conducive to uniform photothermal conversion layers, thus being found to be particularly suited for the fabrication of planographic original plates for CTP use.

[0031] The photothermal conversion material of the invention may contain a binder resin or the like in addition to the phthalocyanine compound of formula (I) which is a light-to-heat converting agent.

[0032] Furthermore, the photothermal conversion material of the invention can be implemented by using the phthalocyanine compound of general formula (I) in combination with various known near-infrared-light absorbing substances within the range not contrary to the objects of the invention.

[0033] The near-infrared-light absorbing materials mentioned above include not only a variety of pigments such as carbon black, aniline black, etc. but also other colors or dyes such as the polymethine dyes (cyanine dyes), phthalocyanine dyes, dithiol metal complex salt dyes, naphthoquinone dyes, anthraquinone dyes, triphenylmethane (analog) dyes, aminium dyes, diimmonium dyes, azo dyes, indoaniline metal complex dyes, intermolecular CT dyes, etc., all of which are described in "Near-Infrared Absorbing Colors" (P45-51), KAGAKU KOGYO (Chemical Industry) (May 1986 issue) and in Chapter 2-2.3 of "The Development and Market Trend of Functional Dyes in the Nineties", CMC (1990). The binder resin is not particularly restricted in kind but includes the homopolymers and copolymers of acrylic monomers such as acrylic acid, methacrylic acid, acrylic esters, methacrylic esters, etc., cellulosic polymers such as methylcellulose, ethylcellulose, cellulose acetate, etc., vinyl polymers and vinyl copolymers such as polystyrene, vinyl chloride-vinyl acetate copolymer, polyvinylpyrrolidone, polyvinyl butyral, polyvinyl alcohol, etc., condensation polymers such as polyesters and polyamides, rubber-like thermoplastic polymers such as butadiene-styrene copolymer etc., and polymers available upon polymerization and crosslinking of photopolymerizable compounds such as epoxy compounds.

[0034] When the photothermal conversion material of the invention is applied to a recording medium such as a laser thermal transfer printing material or a laser thermal recording material, it can be used as formulated with a chromogenic or coloring agent or, as an alternative, a discrete layer containing such a chromogenic or coloring agent may be provided. As the chromogenic or coloring agent, there can be employed sublimable dyes or pigments, electron-donating dye precursors and electron-accepting compounds, polymerizable polymers and various other substances capable of forming images by undergoing physical or chemical change in response to heat which are in use or under development. For example, the coloring agent which can be used in the laser thermal transfer printing material includes but is not limited to inorganic pigments such as titanium dioxide, carbon black, zinc oxide, Prussian blue, cadmium sulfide, iron oxide, and chromates of lead, zinc, barium, and calcium, and organic colors such as azo, thioindigo, anthraquinone, anthoanthrone, triphenldioxane, phthalocyanine, quinacridone, and other dyes. As examples of the dye, acid dyes, direct dyes, dispersed dyes, oil-soluble dyes, and metal-containing oil-soluble dyes can be mentioned.

[0035] The chromogenic agent for use in the laser thermal recording material is not particularly restricted but any of the substances in use in the conventional thermal recording materials can be employed. The electron-donating dye precursor is a compound which donates an electron or accepts the proton of an acid or the like to develop a color and, as such, includes those compounds which have a partial structure such as a lactone, lactam, sultone, spiropyran, ester, or amide structure which undergoes ring-opening or cleavage upon contact with an electron-accepting compound. Thus, for example, triphenylmethane compounds, fluoran compounds, phenothiazine compounds, indolylphthalide

compounds, leucoauramine compounds, rhodamine lactam compounds, triazene compounds, spiropyran compounds, and fluorene compounds can be mentioned. The electron-accepting compound includes phenolic compounds, organic acids and salts thereof, hydroxybenzoic acid esters, and so forth.

[0036] The photothermal conversion material of the invention can be applied with advantage to a planographic original plate for CTP use. The planographic original plate for CTP use comprises a support and, as disposed thereon, a photothermal conversion layer. Optionally a silicone rubber layer may be constructed on the photothermal conversion layer and a protective or other layer may be further provided in superimposition.

[0037] As components of the photothermal conversion layer, there may be an image-forming component in addition to the photothermal conversion material. Alternatively, a layer containing the image-forming component may be built up on the photothermal conversion layer.

[0038] The image-forming component is a material which, when heated, undergoes physical or chemical change to form an image and the variety of materials heretofore proposed or in use can be utilized. For example, the material containing a microencapsulated heat-fusible substance and a binder resin as disclosed in Japanese Kokai Tokkyo Koho H3-108588, the material comprising an active hydrogen-containing binder and a blocked isocyanate on the hydrophilic surface of a support as disclosed in Japanese Kokai Tokkyo Koho S62-164049, the material comprising a microencapsulated lipophilic component and a hydrophilic polymer binder as disclosed in Japanese Kokai Tokkyo Koho H7-1849, the material comprising an acid precursor, a vinyl ether-containing compound and an alkali-soluble resin as disclosed in Japanese Kokai Tokkyo Koho H8-220752, the material comprising a hydroxy-containing macromolecular compound and an o-naphthoquinone diazide compound as disclosed in Japanese Kokai Tokkyo Koho H9-5993, the material containing nitrocellulose etc. as disclosed in Japanese Kokai Tokkyo Koho H9-131977, the material comprising a polymerization initiator and an ethylenically unsaturated monomer, oligomer or macromonomer as disclosed in Japanese Kokai Tokkyo Koho H9-146264, among others. In certain applications, the objective image can be formed by constructing a silicone rubber layer on a photothermal conversion layer (light-sensitive layer or a heat-sensitive recording layer) and, after exposure, bringing the silicone layer into intimate contact or apart as described in Japanese Kokai Tokkyo Koho H9-80745, Kokai Tokkyo Koho H9-131977, and Kokai Tokkyo Koho H9-146264, for instance.

[0039] The planographic original plate for CTP use according to the present invention should have a sufficient degree of flexibility to permit setting on a conventional printing press and, at the same time, have a sufficient strength to withstand the load which may act on it during the printing process. The support, therefore, can be made from many kinds of materials such as paper, plastic (e.g. polyethylene, polypropylene, polystyrene, etc.)-laminated paper, metal sheets made from aluminum (inclusive of its alloys), zinc, copper, etc., and plastic films such as cellulose diacetate, cellulose triacetate, cellulose butyrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, polycarbonate, polyvinyl acetate, etc. As representative supports, coated paper, aluminum or other metal sheets, polyethylene terephthalate or other plastic film, rubber, and their composites can be mentioned. The preferred support material includes aluminum, aluminum alloy, and plastic film. The thickness of the support is 25 μm –3 mm, preferably 100 μm –500 μm .

[0040] The usual process for fabricating a planographic original plate comprises dispersing or dissolving the photothermal conversion material and image-forming component in a solvent and coating a support with the dispersion or solution.

[0041] The solvent which can be used in this process includes water, alcohols such as methyl alcohol, isopropyl alcohol, isobutyl alcohol, cyclopentanol, cyclohexanol, diacetone alcohol, etc., cellosolves such as methylcellosolve, ethylcellosolve, etc., aromatic hydrocarbons such as toluene, xylene, chlorobenzene, etc., esters such as ethyl acetate, butyl acetate, isoamyl acetate, methyl propionate, etc., ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, etc., chlorinated hydrocarbons such as methylene chloride, chloroform, trichloroethylene, etc., ethers such as tetrahydrofuran, dioxane, etc., and aprotic polar solvents such as N,N-dimethylformamide, N-methylpyrrolidone, and so forth.

[0042] For improved adhesion and printing quality, a subbing (undercoat) layer may be interposed between the support and the photothermal conversion layer or the support itself may be surface-treated. The subbing layer may for example be a light-sensitive polymer layer photocured prior to construction of the photothermal conversion layer as disclosed in Japanese Kokai Tokkyo Koho S60-22903, the heat-cured epoxy resin layer disclosed in Japanese Kokai Tokkyo Koho S62-50760, the cured gelation film disclosed in Japanese Kokai Tokkyo Koho S63-133151, the layer formed by using a urethane resin and a silane coupling agent as disclosed in Japanese Kokai Tokkyo Koho H3-200965, and the urethane resin layer disclosed in Japanese Kokai Tokkyo Koho H3-273248.

[0043] To provide a protective film for the purpose of protecting the surface of said photothermal conversion layer or silicone rubber layer, a transparent film such as polyethylene, polypropylene, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol, polyethylene terephthalate, or cellophane film may be laminated or such a film may be drawn and used.

[0044] To fabricate a planographic printing plate, the above planographic original plate for CTP use is irradiated with the light of a semiconductor laser having an emission band of 750–900 nm in the per se known manner.

EXAMPLES

[0045] The following examples are intended to illustrate the present invention in further detail and should by no means be construed as defining the scope of the invention.

Example 1

[0046] A polyethylene terephthalate (PET) film with an average thickness of 5 μm is coated with a solution containing 10 g of the binder Delpet 80N (acrylic resin, Asahi Chemical Industry) and 0.2 g of Compound No. 34 (Table 1) in 90 g of toluene-methyl ethyl ketone (1:1) using a wire bar in a dry film thickness of about 5 μm to provide a sample.

[0047] A single-mode semiconductor laser (wavelength 830 nm) and optics were disposed so as to provide a condensed laser beam with a diameter of 10 μm on the surface of said sample. The semiconductor laser was set so as to permit variation of the power of laser light reaching the surface over the range of 50–200 mW and the sample was irradiated with the single pulse at the pulse width of 20 μs . After completion of the irradiation, the sample was examined under the light microscope. As a result, a through-hole with a diameter of about 10 μm was formed when the power of laser light reaching the surface was 70 mW.

Example 2

[0048] Except that 0.2 g of Compound No. 93 (Table 1) was used in lieu of Compound No. 34 (Table 1), the procedure of Example 1 was otherwise repeated. Examination of the irradiated sample under the light microscope revealed that a through-hole with a diameter of about 10 μm was formed when the power of laser light reaching the surface was 80 mW.

Example 3

[0049] A polyethylene terephthalate (PET) film having an average thickness of 5 μm was coated with a solution containing 10 g of the binder Delpet 80N (acrylic resin, Asahi Chemical Industry) and 0.2 g of Compound No. 27 (Table 1) in 90 g of toluene-methyl ethyl ketone (1:1) using a wire bar in a dry film thickness of about 5 μm to provide a sample.

[0050] A single-mode semiconductor laser (wavelength 790 nm) and optics were disposed so as to provide a condensed laser beam with a diameter of 10 μm on the surface of said sample. The semiconductor laser was set so as to permit variation of the power of laser light reaching the surface over the range of 50–200 mW and the sample was irradiated with the single pulse at the pulse width of 20 μs . After completion of the irradiation, the sample was examined under the light microscope. As a result, a through-hole with a diameter of about 10 μm was formed when the power of laser light reaching the surface was 70 mW.

Example 4

[0051] Except that 0.2 g of Compound No. 36 (Table 1) was used in lieu of 0.2 g of Compound No. 27 (Table 1), the procedure of Example 3 was otherwise repeated. As a result, a through-hole with a diameter of about 10 μm was formed when the power of laser light reaching the surface was 80 mW.

Example 5

Formation of a subbing layer

[0052] As the undercoat on a polyethylene terephthalate film having a thickness of 175 μm , a gelatin subbing layer was constructed in a dry film thickness of 0.2 μm .

Formation of a photothermal conversion layer

[0053] A coating dope according to the following recipe was applied over the above gelatin-coated polyethylene terephthalate film in a dry film thickness of 2 μm to provide a photothermal conversion layer.

	Parts by weight
Compound No. 34 (Table 1)	0.1
Crisvon 3006 LV (polyurethane; Dainippon Ink and Chemicals)	5.0

(continued)

	Parts by weight
Solsperse S27000 (ICI)	0.4
Nitrocellulose (n-propanol 30% contained)	4.2
Xylylenediamine (1 mol)-glycidyl methacrylate (4 mol) adduct	2.0
Ethyl Michler's ketone	0.2
Tetrahydrofuran	90

Formation of a silicone rubber layer

[0054] A coating dope conforming to the following recipe was applied over the above photothermal conversion layer in a dry film thickness of 2 μm to provide a silicone rubber layer.

	Parts by weight
α , ω -Divinylpolydimethylsiloxane (deg. of polymerization: ca 700)	9.0
$(\text{CH}_3)_3\text{Si}-\text{O}-(\text{SiH}(\text{CH}_3)-\text{O})_8-\text{Si}(\text{CH}_3)_3$	0.6
Polydimethylsiloxane (deg. of polymerization: ca 8000)	0.5
Olefin-chloroplatinate	0.08
Inhibitor $\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_3$	0.07
Isopar G (Esso Chemical)	55

[0055] Using the planographic original plate obtained above, writing was performed using a semiconductor laser with a beam diameter of 10 μm and an emission wavelength of 830 nm under the conditions that the power on the plate surface was 110 mW. The laser recording sensitivity was 200 mJ/cm² and the resolution was 8 μm . Thus, a planographic printing plate with sharp edges could be obtained.

Example 6

[0056] Except that 0.1 part by weight of Compound No. 93 (Table 1) was used in lieu of 0.1 part by weight of Compound No. 34 (Table 1), the procedure of Example 5 was otherwise repeated to provide a planographic original plate.

[0057] Using the planographic original plate obtained above, writing was performed using a semiconductor laser with a beam diameter of 10 μm and an emission wavelength of 830 nm under the conditions that the power on the plate surface was 110 mW. The laser recording sensitivity was 200 mJ/cm² and the resolution was 8 μm . Thus, a planographic printing plate with sharp edges could be obtained.

Example 7

[0058] Except that 0.1 part by weight of Compound No. 27 (Table 1) was used in lieu of 0.1 part by weight of Compound No. 34 (Table 1), the procedure of Example 5 was otherwise repeated to provide a planographic original plate.

[0059] Using the planographic original plate obtained above, writing was performed using a semiconductor laser with a beam diameter of 10 μm and an emission wavelength of 790 nm under the conditions that the power on the plate surface was 110 mW. The laser recording sensitivity was 200 mJ/cm² and the resolution was 8 μm . Thus, a planographic printing plate with sharp edges could be obtained.

Example 8

[0060] Except that 0.1 part by weight of Compound No. 43 (Table 1) was used in lieu of 0.1 part by weight of Compound No. 34 (Table 1), the procedure of Example 5 was otherwise repeated to provide a planographic original plate.

[0061] Using the planographic original plate obtained above, writing was performed using a semiconductor laser with a beam diameter of 10 μm and an emission wavelength of 830 nm under the conditions that the power on the plate surface was 110 mW. The laser recording sensitivity was 200 mJ/cm² and the resolution was 8 μm . Thus, a planographic printing plate with sharp edges could be obtained.

Example 9

[0062] Except that 0.1 part by weight of Compound No. 136 (Table 1) was used in lieu of 0.1 part by weight of Compound No. 34 (Table 1), the procedure of Example 5 was otherwise repeated to provide a planographic original plate.

[0063] Using the planographic original plate obtained above, writing was performed using a semiconductor laser with a beam diameter of 10 μm and an emission wavelength of 830 nm under the conditions that the power on the plate surface was 110 mW. The laser recording sensitivity was 200 mJ/cm² and the resolution was 8 μm . Thus, a planographic printing plate with sharp edges could be obtained.

Example 10

[0064] Except that 0.1 part by weight of Compound No. 137 (Table 1) was used in lieu of 0.1 part by weight of Compound No. 34 (Table 1), the procedure of Example 5 was otherwise repeated to provide a planographic original plate.

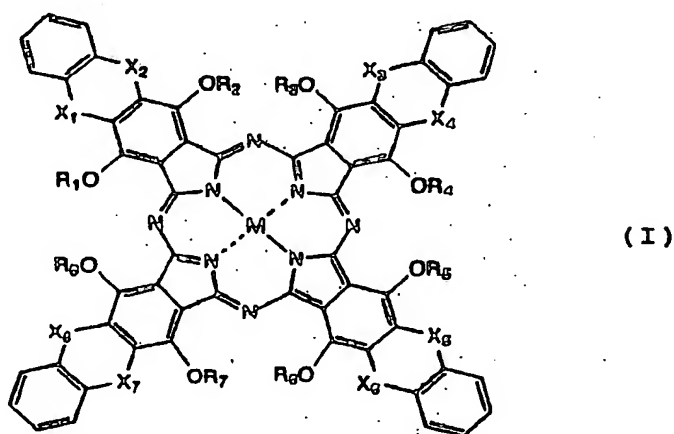
[0065] Using the planographic original plate obtained above, writing was performed using a semiconductor laser with a beam diameter of 10 μm and an emission wavelength of 830 nm under the conditions that the power on the plate surface was 110 mW. The laser recording sensitivity was 200 mJ/cm² and the resolution was 8 μm . Thus, a planographic printing plate with sharp edges could be obtained.

EFFECT OF THE INVENTION

[0066] The photothermal conversion material of the present invention shows high sensitivity to the light of a semiconductor laser having an emission frequency band in the near-infrared region (750 nm ~ 900 nm) of the spectrum and high photothermal conversion efficiency so that it can be used in a variety of applications. Moreover, the original plate for CTP use which incorporates this photothermal conversion material is easy to fabricate and provides prints with high image quality.

Claims

1. A photothermal conversion material comprising a phthalocyanine compound of the following general formula (I)



wherein R_1 – R_8 each represents alkyl or alkoxyalkyl; X_1 – X_8 each represents sulfur or NR_9 ; X_1 = (either X_3 or X_4) = (either X_5 or X_6) = (either X_7 or X_8) = sulfur and X_2 = (the other one of X_3 and X_4) = (the other one of X_5 and X_6) = (the other one of X_7 and X_8) = NR_9 ; R_9 represents hydrogen or alkyl; M represents a couple of hydrogen atoms, a divalent metal, a trivalent metal derivative, or a tetravalent metal derivative.

2. The photothermal conversion material according to Claim 1 wherein M in general formula (I) is Co, Ni, Cu, Zn, VO, or TiO.

3. The photothermal conversion material according to Claim 1 or 2 wherein each of R_1 ~ R_8 in general formula (I) is a straight-chain or branched alkyl group containing 1~12 carbon atoms or an alkoxyalkyl group containing a total of 2~6 carbon atoms.
- 5 4. The photothermal conversion material according to any of Claims 1~3 wherein R_9 in general formula (I) is hydrogen or a straight-chain or branched alkyl group containing 1~12 carbon atoms.
5. A planographic original plate for CTP use which comprises a support and, as disposed thereon, a photothermal conversion layer containing the photothermal conversion material claimed in Claim 1.
- 10 6. A method of fabricating a planographic printing plate which comprises preparing the planographic original plate of Claim 5 and irradiating the plate using a semiconductor laser having an emission band of 750 nm ~ 900 nm as a light source.

(19)



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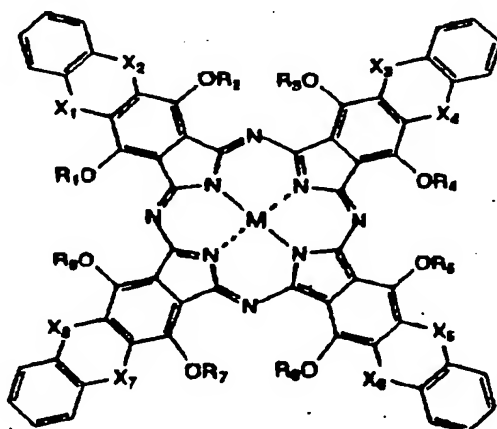
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(54) **Photothermal conversion material and planographic printing plate derived therefrom**

(57) A photothermal conversion material showing high sensitivity to the light of a semiconductor laser having an emission frequency band of 750 nm ~ 900 nm with a high photothermal conversion efficiency and a planographic original plate fabricated by using the transducer are provided. This photothermal conversion material comprises a phthalocyanine compound of the following general formula (I)



(I)

wherein $R_1 \sim R_8$ each represents alkyl or alkoxyalkyl; $X_1 \sim X_8$ each represents sulfur or NR_9 , where R_9 is hydrogen or alkyl.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X,D	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 07, 31 July 1996 (1996-07-31) & JP 08 060008 A (YAMAMOTO CHEM INC;MITSUI TOATSU CHEM INC), 5 March 1996 (1996-03-05) * abstract *	1-4	B41M5/40 B41M5/24 B41C1/10 C09B69/10 G11B7/24
Y		5,6	
X	EP 0 782 164 A (MITSUI TOATSU CHEMICALS ;YAMAMOTO CHEMICALS INC (JP)) 2 July 1997 (1997-07-02) * page 2, line 46 - line 52 * * page 3, line 34 - line 59 * * page 6, line 47 - page 9, line 2 * * example 11, formula (11) *	1-4	
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 04, 30 April 1997 (1997-04-30) & JP 08 317737 A (MITSUI TOATSU CHEM INC), 3 December 1996 (1996-12-03) * abstract * * page (13), formula 11 *	1-4	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G11B B41C B41M C09B
X	CHEMICAL ABSTRACTS, vol. 125, no. 18, 28 October 1996 (1996-10-28) Columbus, Ohio, US; abstract no. 224557, MASAOKA, TOSHIHIRO ET AL: "Manufacture of phthalocyanines as near IR-absorbing materials and their precursor phthalonitriles" XP002126055 * abstract * & JP 08 176101 A (YAMAMOTO CHEMICALS INC, JAPAN;MITSUI TOATSU CHEMICALS) 9 July 1996 (1996-07-09) -/-	1-4	
The present search report has been drawn up for all claims			
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CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons S: member of the same patent family, corresponding document	

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DOCUMENTS CONSIDERED TO BE RELEVANT			
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Y	EP 0 802 067 A (TORAY INDUSTRIES) 22 October 1997 (1997-10-22) * page 2, line 5 - page 3, line 28 * * page 7, line 27 - line 37 * * page 9, line 2 - line 18 * * examples 10-13 *	5,6	
D	& JP 09 131977 A -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 December 1999	Examiner Markham, R
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background C : non-written disclosure P : intermediate document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 30 9455

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-12-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 08060008 A	05-03-1996	NONE	
EP 0782164 A	02-07-1997	JP 9230134 A	05-09-1997
		US 5804102 A	08-09-1998
		JP 10078509 A	24-03-1998
JP 08317737 A	03-12-1996	DE 69600274 D	10-06-1998
		DE 69600274 T	01-10-1998
		EP 0732049 A	18-09-1996
		ES 2116796 T	16-07-1998
		US 5953857 A	21-09-1999
JP 8176101 A	09-07-1996	NONE	
EP 0802067 A	22-10-1997	JP 9131976 A	20-05-1997
		JP 9131977 A	20-05-1997
		JP 9131978 A	20-05-1997
		JP 9131979 A	20-05-1997
		JP 9131980 A	20-05-1997
		JP 9131981 A	20-05-1997
		JP 9150589 A	10-06-1997
		JP 10039497 A	13-02-1998
		AU 7507196 A	29-05-1997
		CA 2209831 A	15-05-1997
		WO 9717208 A	15-05-1997

EPO FORM P469

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82